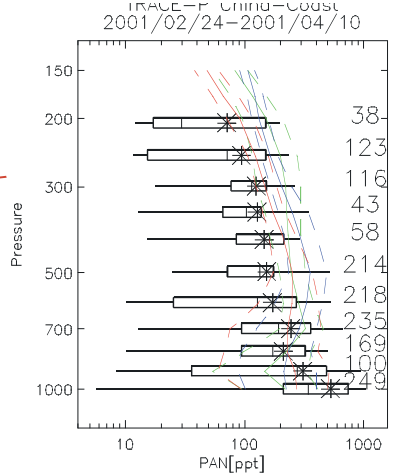
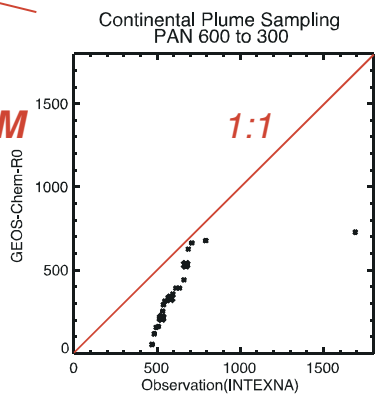
The *RIDDLES* of Acetaldehyde and PAN MIS-Estimation *in the GMI -Trop. Models* and *in a Broader INTEX-NA Simulation Set*



Every Meteor.-Set Overestimates

- *Meteorological Simulation Does Really Matter in the Tropospheric NOy Budget,*
- *So Does Chemical Mechanism?*

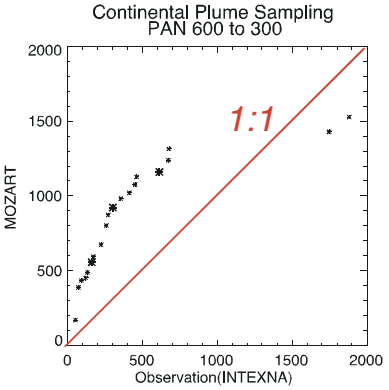
GEOS-CHEM

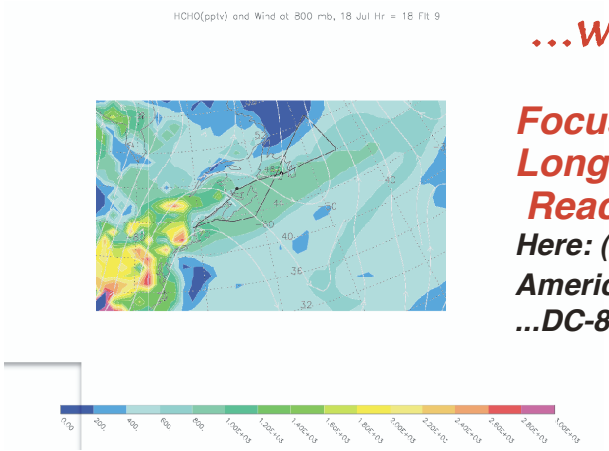


Robert Chatfield
NASA, ARC

...with a lot of help

MOZART





Focus of the presentation:
Long Plumes of
Reacting Continental Organics

Here: (HCHO) Plume Flowing out from North America (INTEX-NA)
...DC-8 Track is shown

Which do you like?

Thanks to ...

Robert B. Chatfield ***NASA (Ames)***
Robert Esswein ***chatfield@clio.arc.nasa.gov***

Francis Binkowski ***UNC-CEP***
Saravanan Arunchalam

GMI Modeling team

Al Fried ***NCAR***
Donald Blake ***UC-Irvine***
Many INTEX-NA Experimenters
Brune, Shetter,

Rohit Mathur ***EPA (formerly CEP)***

with thanks to ...

Langley Theory Team
including Jim Crawford, Jennifer Olson

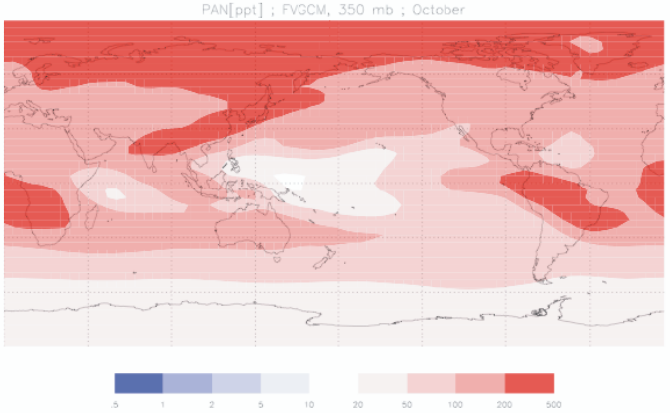
Harvard Geos-Chem Team
including Rynda Hudman, Daniel Jacob

MOZART-INTEX-NA Team at NCAR:
esp. Peter Hess
and Larry Horowitz, GFDL

NOAA NARE-97 Team including
Michael Trainer ***NOAA Aeronomy***
Paul Goldan
James Roberts
William Koster

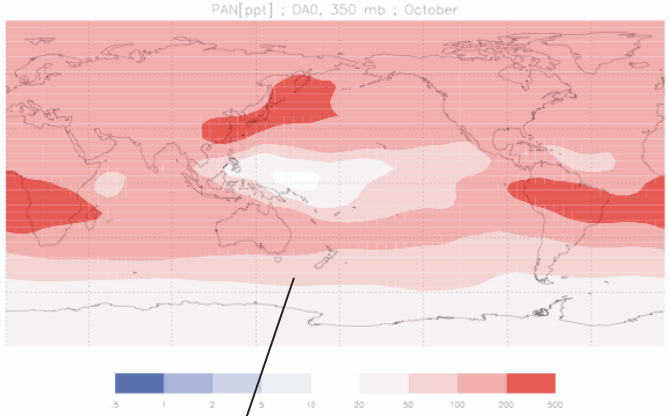
Transport Aspects of the PAN Distribution *Southern Spring*

FVGCM



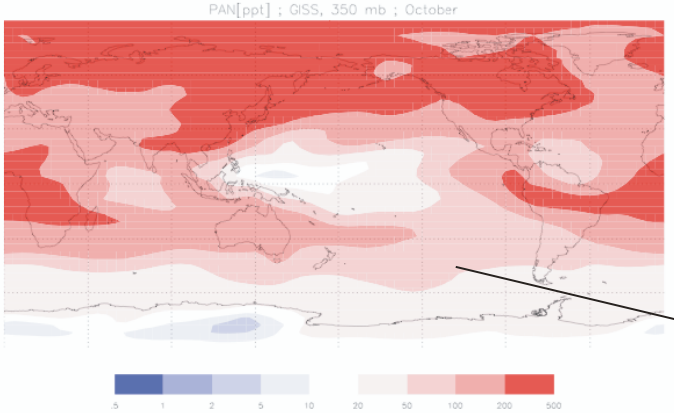
Most spatial detail
poor Cb transport
tight tropopause

DAO



Good Cb transport

GISS

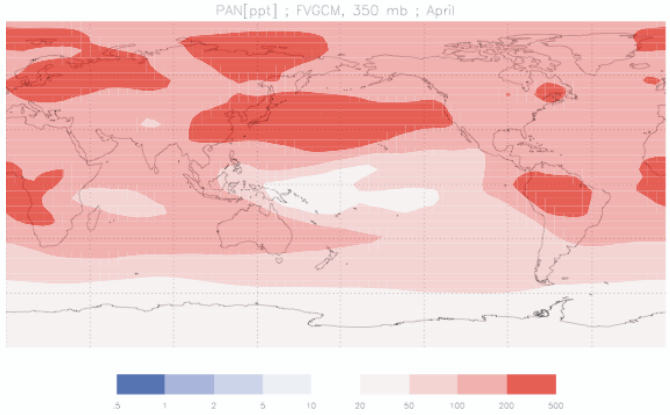


Good Cb transport
much trop-strat mixing

shoupage

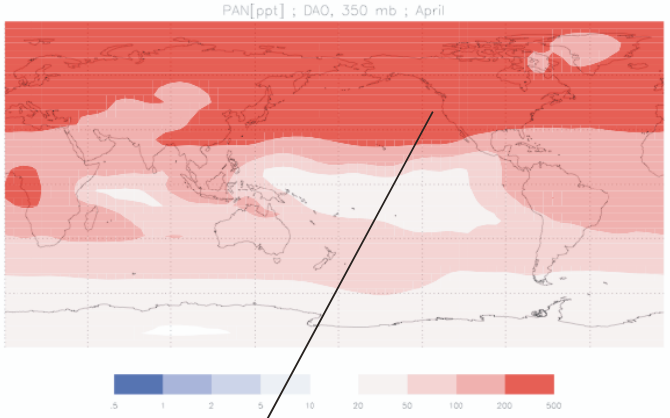
Northern Spring

FVGCM



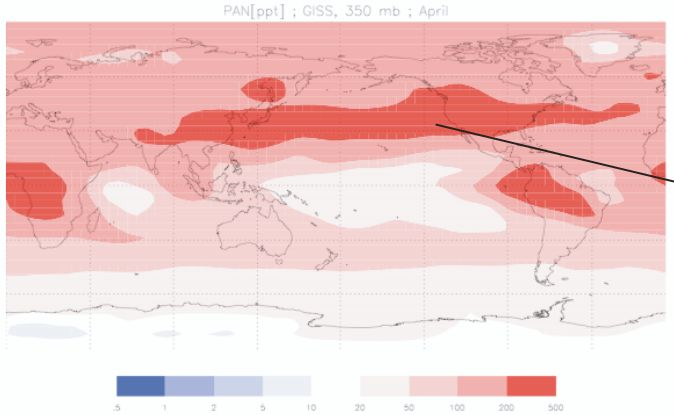
DAO

Good Cb transport



GISS

Too much trop-strat mixing



Good Cb transport

showpage

Major reasons why PAN levels differ with GMI meteorologies: Transport effects which modify UT distributions

5. Mixing: inadequate tropopause.

4. Winds: Jet Strengths

6. Temparature variability along path.

3. Diffusion in the UT

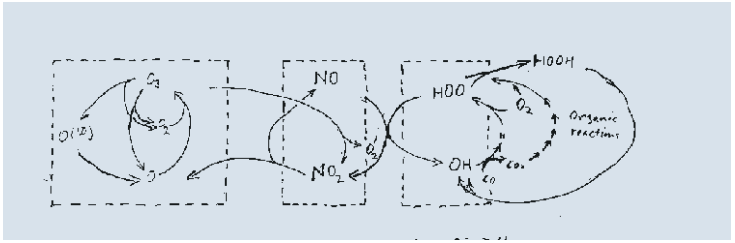
2 Cb-Cloud Transport

1. Dispersion of near-surface emissions

Peroxy Acetyl Nitrate, Aldhydes, and Global Ozone:

Ozone levels in the Global Troposphere:

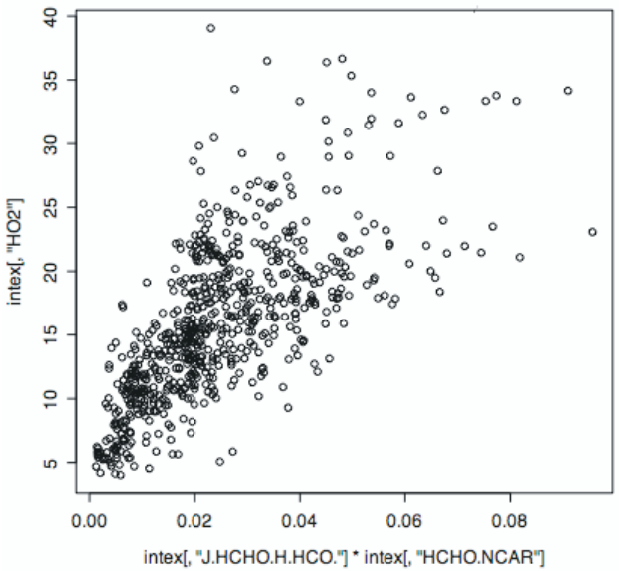
Transport of Peroxy Radical and NO Reservoirs allows continuing O_3 production



$ROO + NO \Rightarrow RO + NO_2$

NO reservoirs in the remote troposphere: PAN and HNO_3
PAN active at ~5 C and above (600 mb and below)
HNO_3 active in uppermost troposphere (200 mb and above)

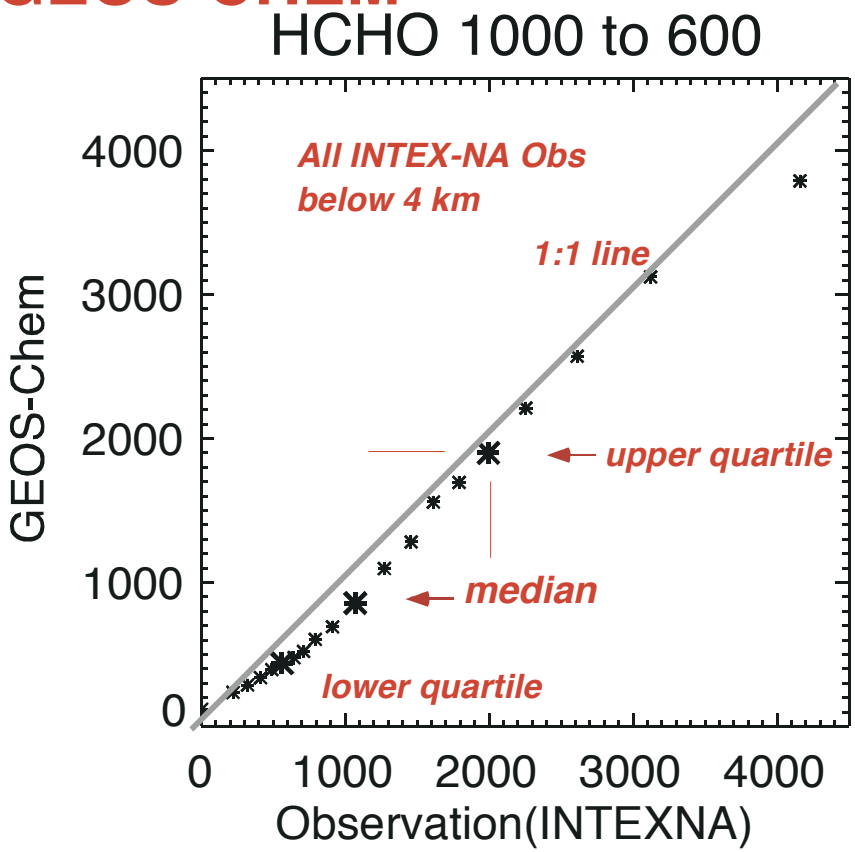
Indicators of ROO production: the aldehydes:



INTEX-NA data: correlation of formaldehyde reaction rate and HO_2 peroxy radical abundance

Q-Q plots of the statistical distribution

GEOS-CHEM



Quantile-Quantile or *Q-Q* plots:
quartile vs. quartile, median vs median, max vs max
... plumes distinguished from "background"

A statistical comparison only, not a point-by-point:
NO time-space matching except
that we use the same aircraft locations and times

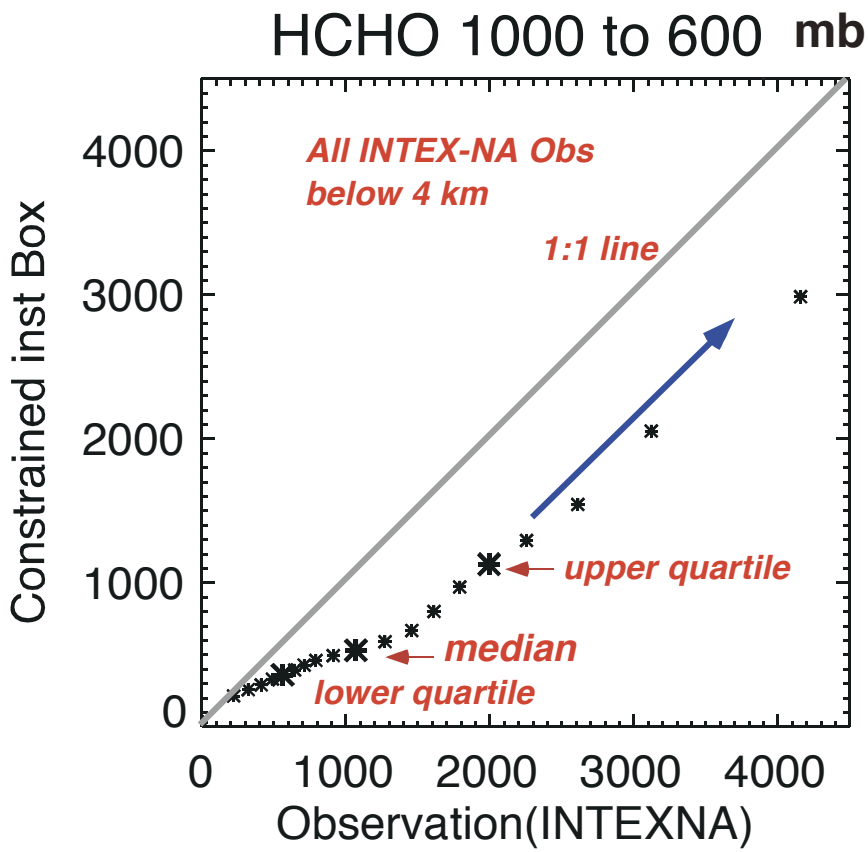
We expect that the model
- *misses features in detail, but*
- *tends to get generally the same suite of features*

Applicability and Expectations of Matching for Q-Q plots:

Point-model comparisons > Assimilation model > Forecast/Reanalysis model > Same date/location

INTEX-NA runs

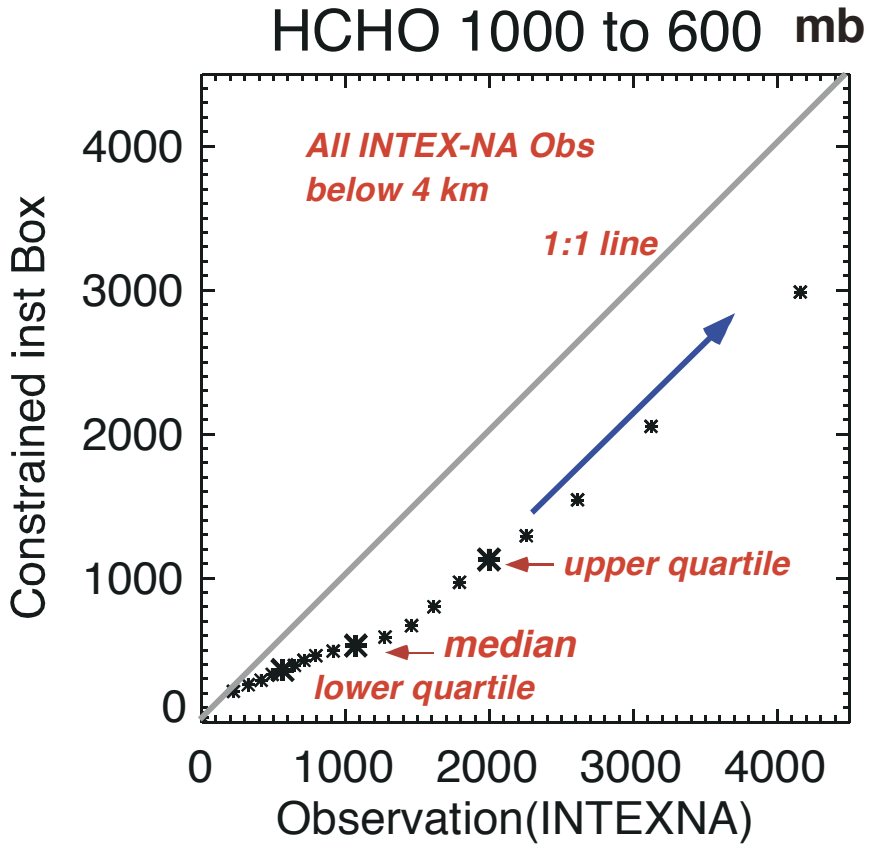
GEOS-CHEM runs

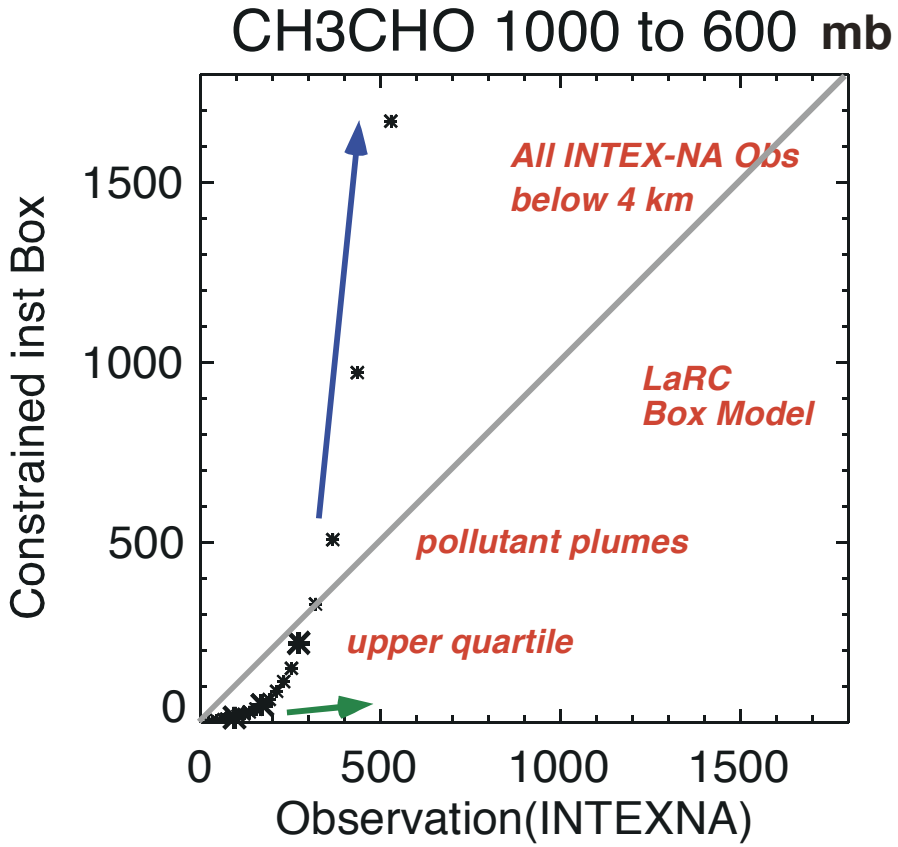


These box-model calculations made for all aircraft samples of the composition measured by the DC-8 the new INTEX-NA dataset by the Crawford-Olson NASA Langley group. Thanks to Jennifer for comments.

Formaldehyde concentrations cannot be satisfactorilycalculated based on observed hydrocarbons (which account for most primary emissions, or the oxidized organics observed away from sources.

These box-model calculations made for all aircraft samples of the composition measured by the DC-8 the new INTEX-NA dataset by the Crawford-Olson NASA Langley group illustrate a





An interpretation of this line: Mechanism responds to pollution "source loading" (largely hydrocarbon) but cannot respond to *unobservable* pollutant-plume oxidized-organic loading

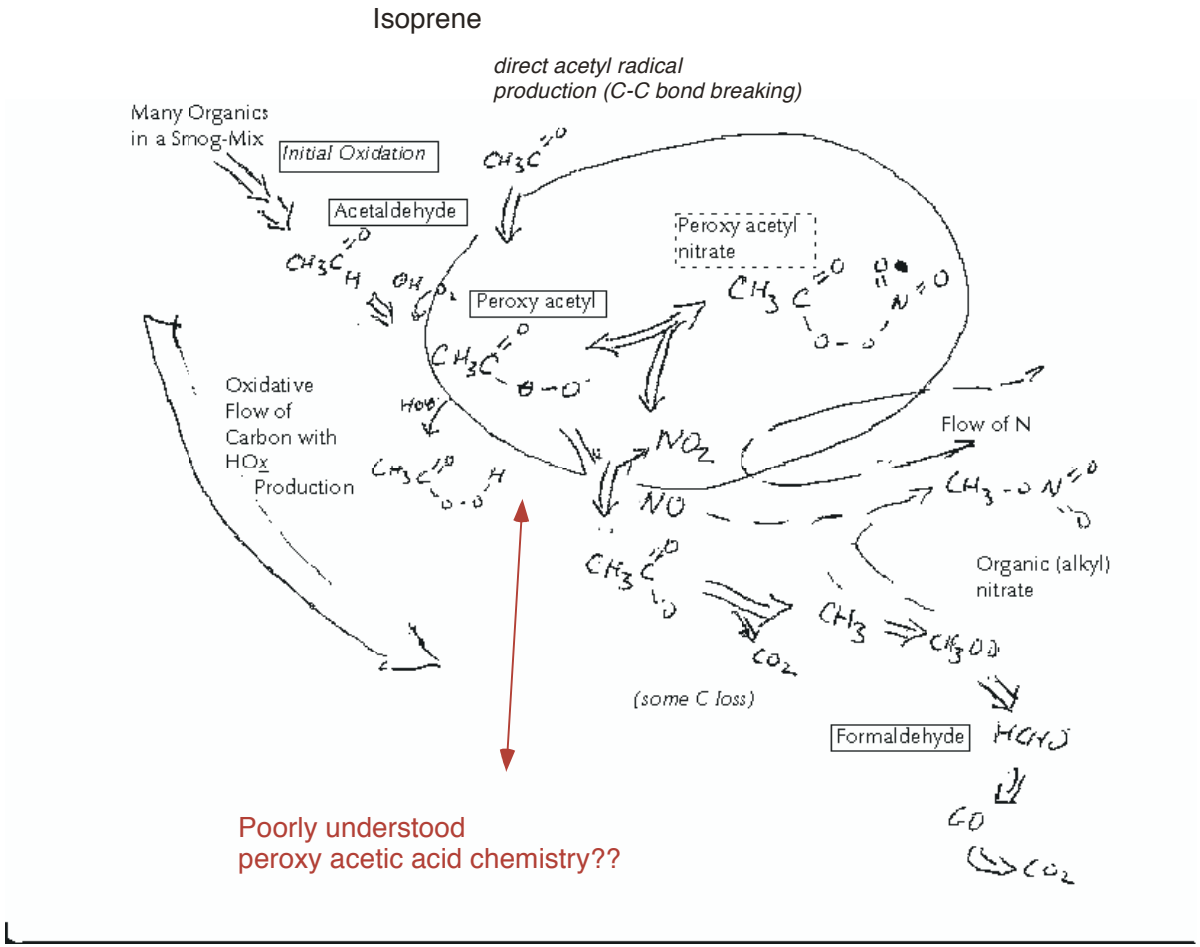
.

One interpretation of this line: H. Singh's (and other) instruments respond to an artifact below 150 ppt

Another: there is an unknown source

An interpretation of this line: Mechanism responds to pollution "source loading" but with too great an acetaldehyde yield.

PAN and Reaction Mechanisms: Lessons from INTEX-NA

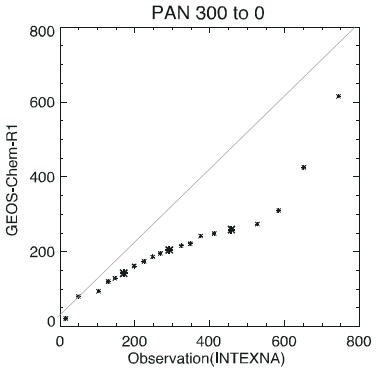


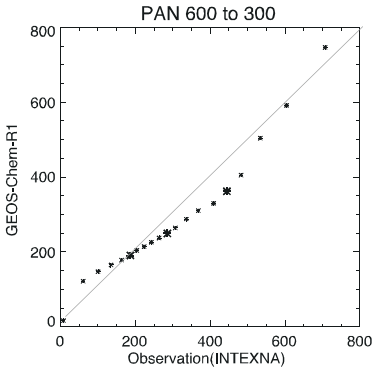
Simple aldehydes and PAN "gauge" the oxidation chain and the flow of reactive *C - H* "fuel"

Simulation of PAN by GEOS-CHEM and MOZART
By altitude band

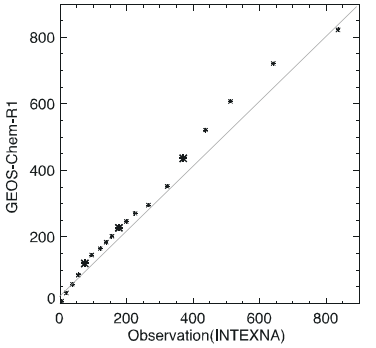
GEOS-CHEM

freeze-out region



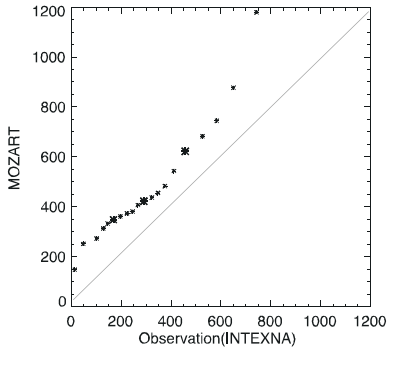


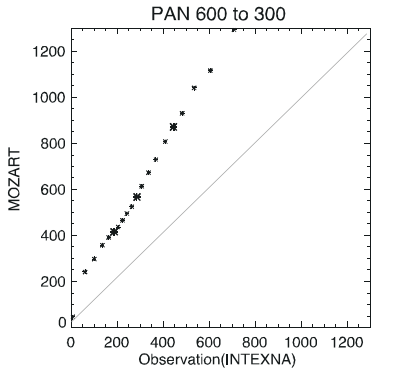
Active region



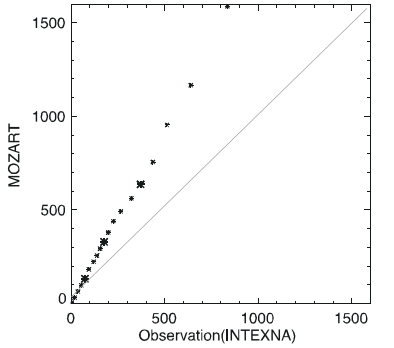
MOZART

freeze-out region

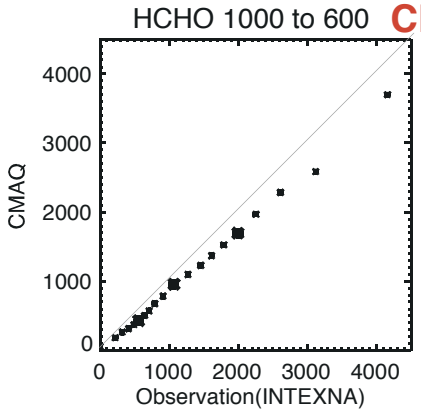




Active region



Simulation of HCHO by GEOS-CHEM and MOZART



CMAQ: MM5-SAPRC

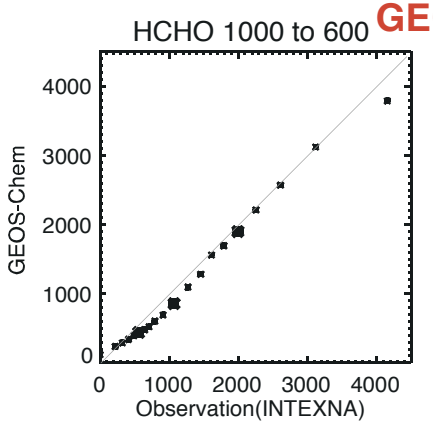
Community Model for Air Quality: EPA

(run at UNC)

closest to a normative regional model,

... but with SAPRC chemistry (mistake??)

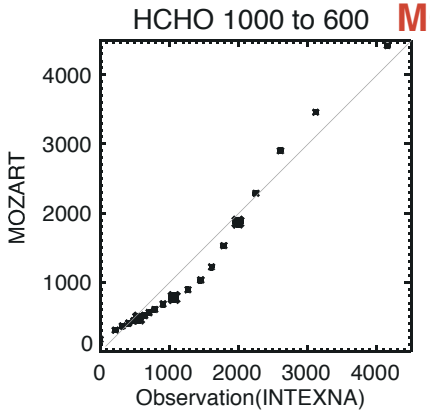
good, low VOC emissions?



GEOS-CHEM

"R1 INTEX-NA run"

right on

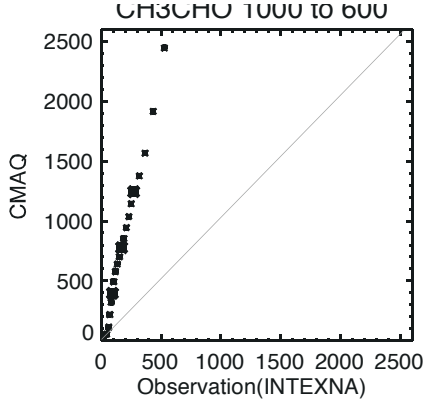


MOZART

Good: what do inflections tell us?EPAEPA

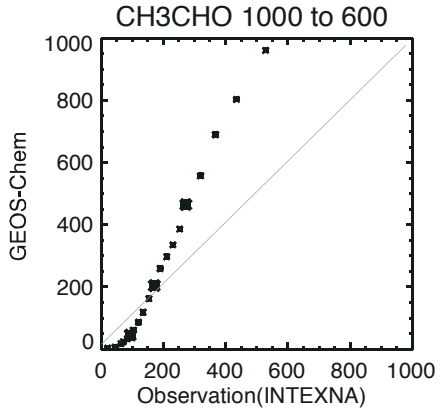
Simulation of Acetaldehyde by GEOS-CHEM

CMAQ: MM5-SAPRC



Extreme overprediction... SAPRC mechanism ... C-bond, RACM2

GEOS-CHEM

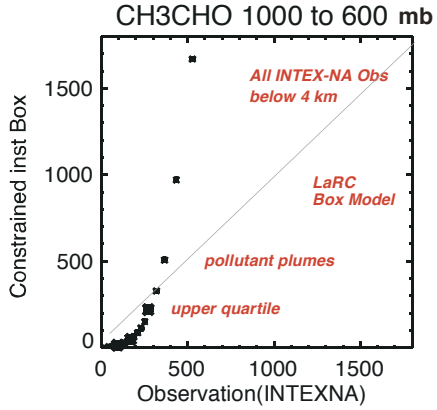


Merely worrisome

Formaldehyde/acetaldhyde results explained:

- Mechanisms emphasize C-H bond scission (abstraction)

(Langley Point Model)



Very large, unlike HCHO: mechanism over-comes "low source stock"

over C-C bond scission (alkoxy decomposition)

- Fundamental lab chemistry may be unclear
- Schemes probably differ

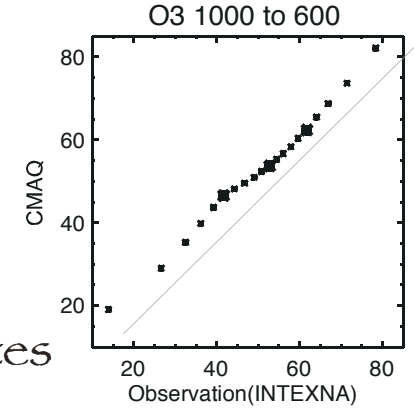
Simulation of Ozone

by CMAQ, GEOS-CHEM, MOZART

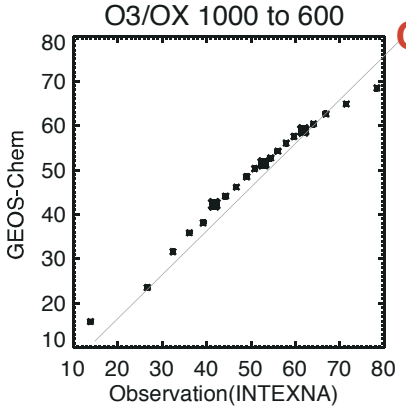
lower limit O_3;

extremely visible

at land-surface sites



CMAQ: MM5-SAPI

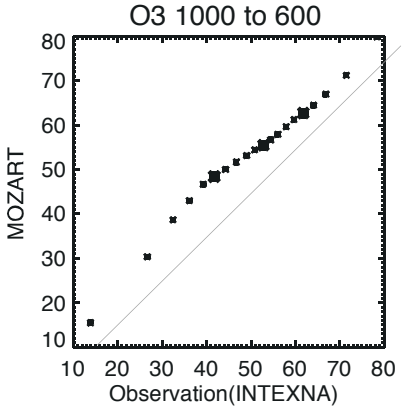


GEOS-CHEM

misses

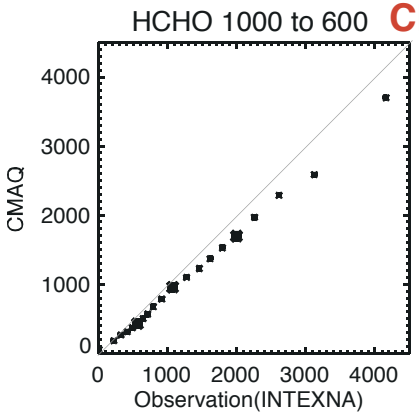
big peaks

cf GEOS-CHEM PAN

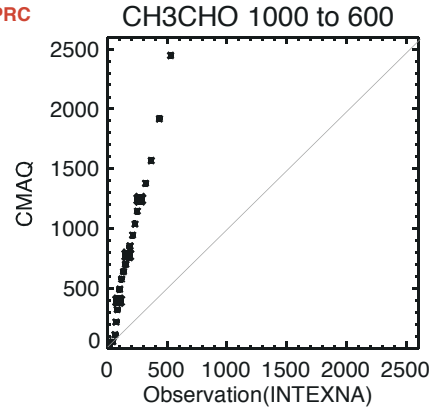


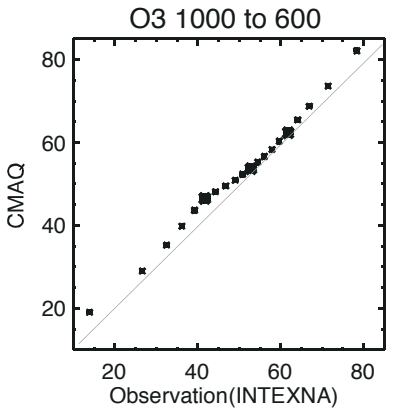
MOZART

lower limit



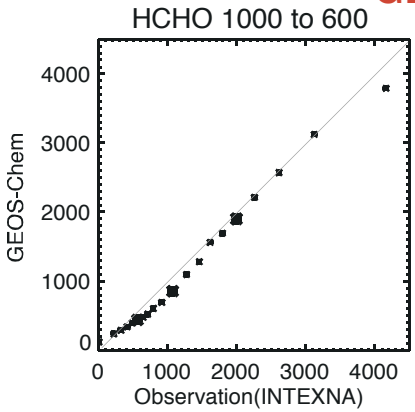
CMAQ: MM5-SAPRC

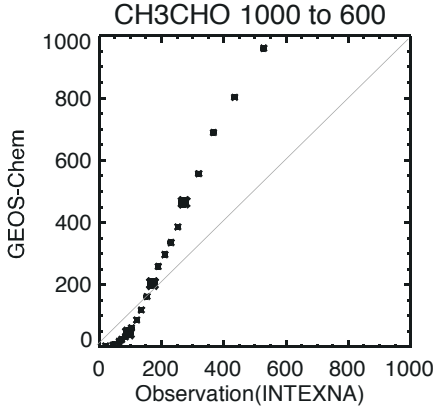


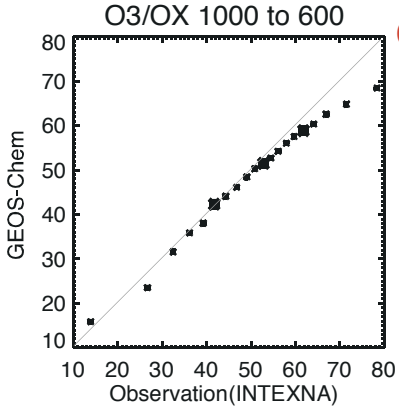


CMAQ: MM5-SAPRC

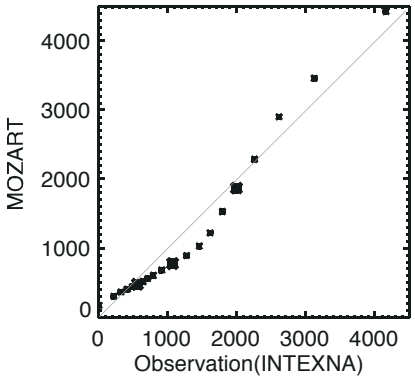
GEOS-CHEM



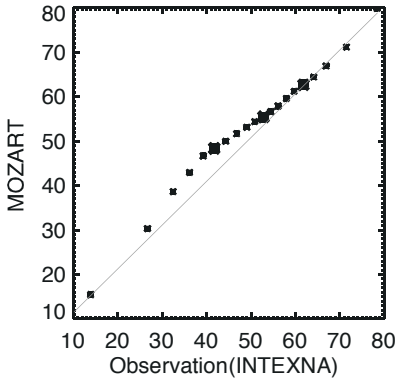




GEOS-CHEM

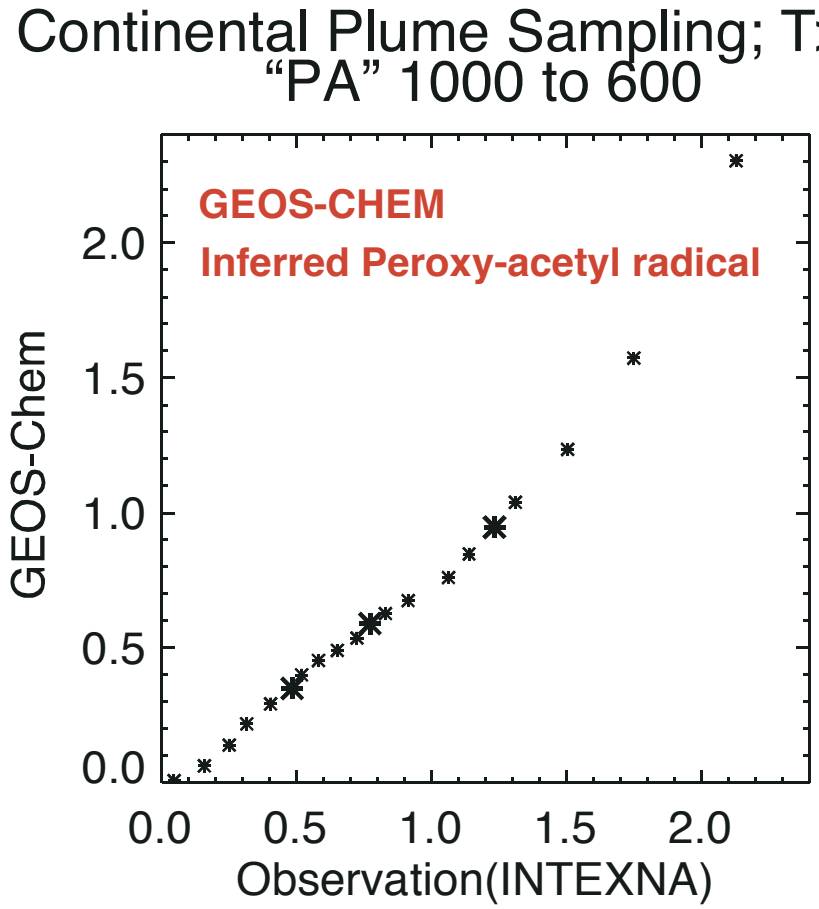


MOZART



MOZART

"Central" PAN decomposition / reformation chemistry appears to be valid

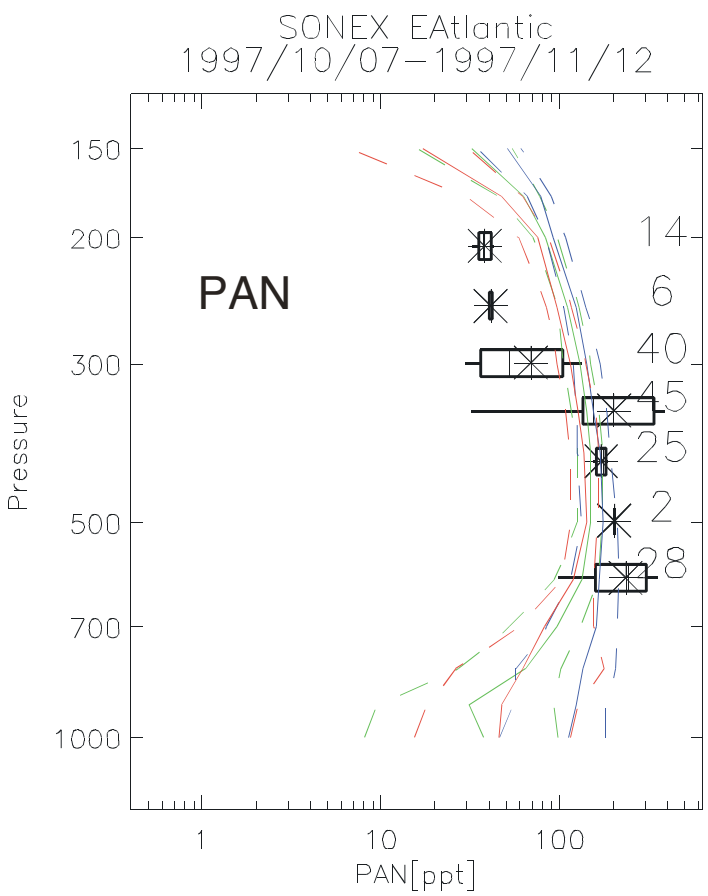


$$PA = f(T)\,\frac{[PAN]}{[NO_2]}$$

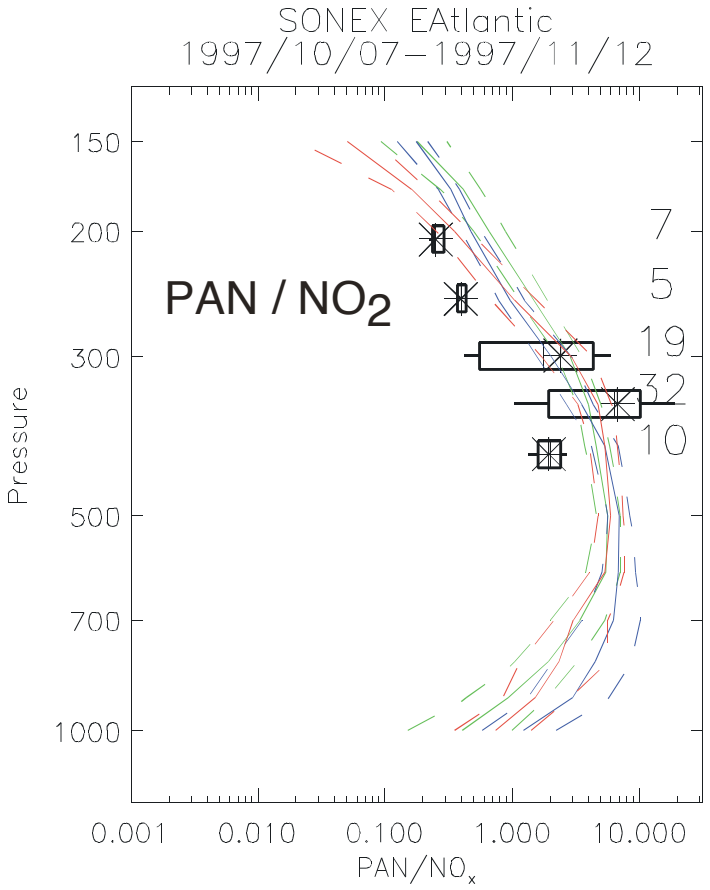
The peroxy-acetyl radical / PAN balance seems

- to be well characterized by laboratory data and
- not disturbed by PAA, with poorly understood chemistry

All three models show similar over-prediction in North Atlantic



Similar chemistry?



DAO-97 FVGCM GISS

median ——— ——— ———

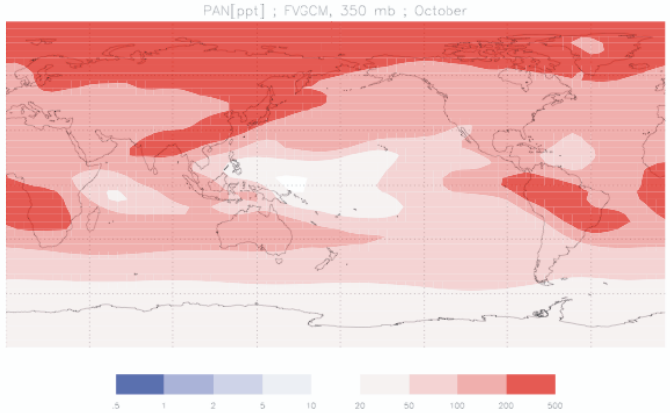
quartiles – – – – – –

DAO-1997 may be for actual tiime period ....does not seem to help simulation.

Want "Aura" runs for INTEX-NA

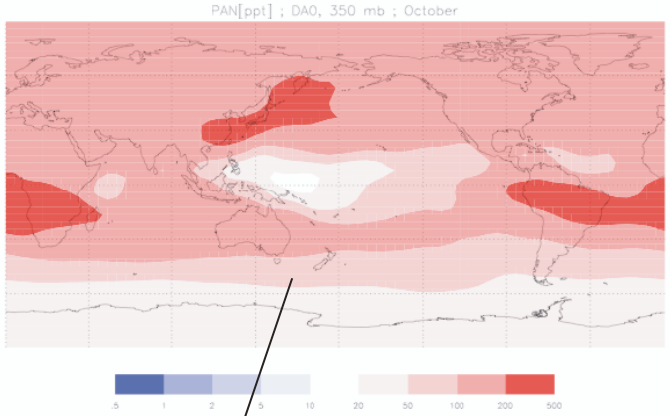
REPRISE: Transport Aspects of the PAN Distribution

FVGCM



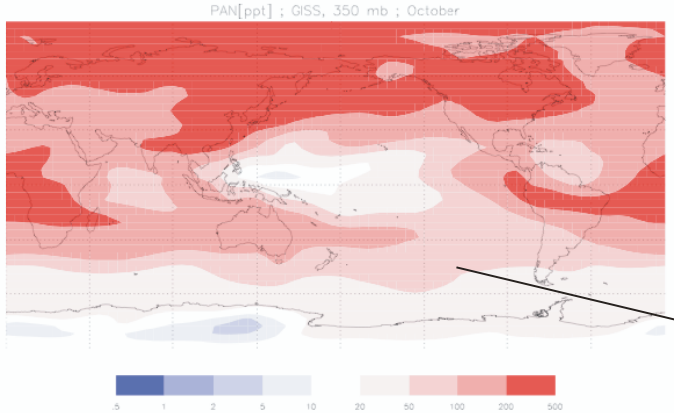
Most spatial detail
poor Cb transport
tight tropopause

DAO



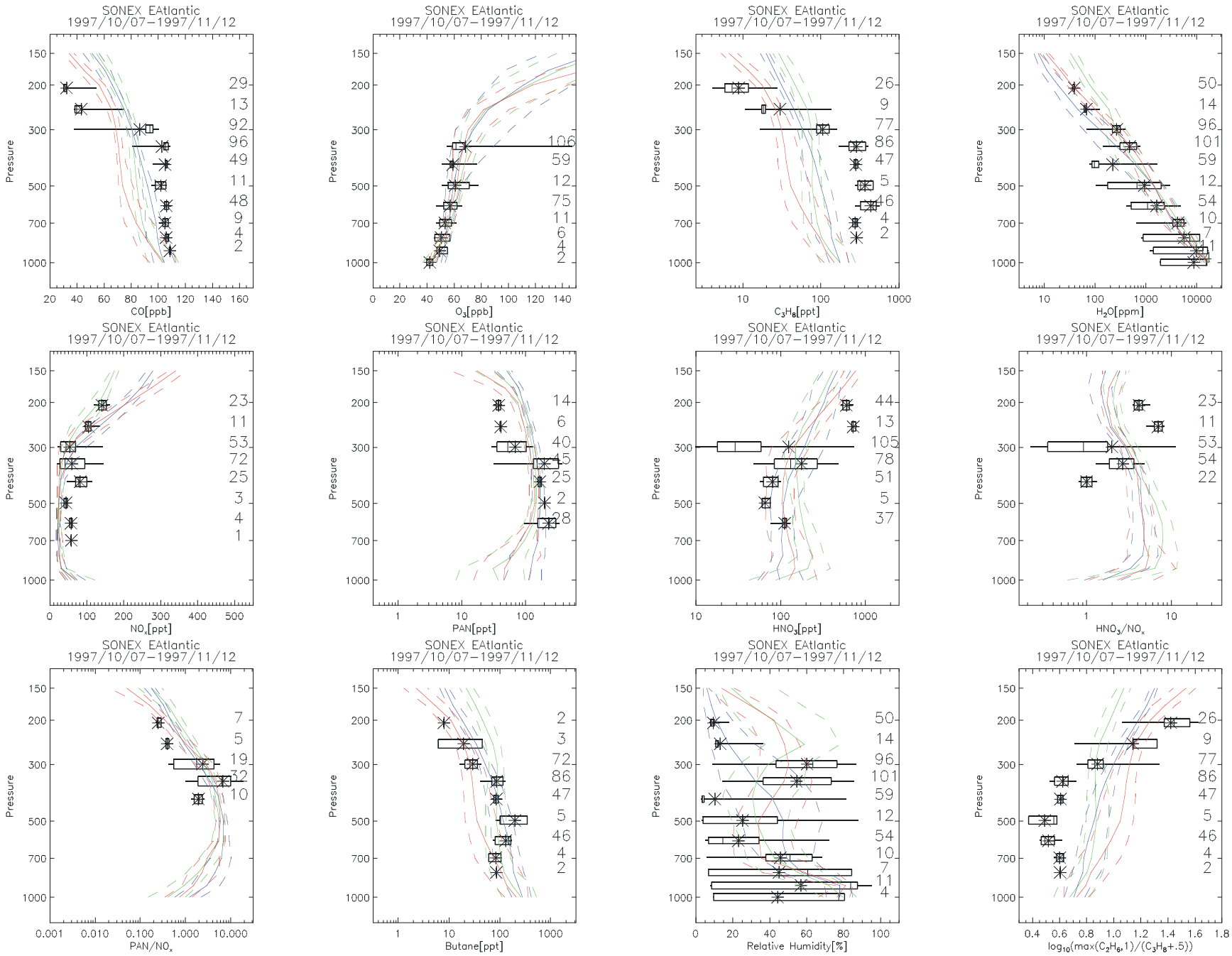
Good Cb transport

GISS



Good Cb transport
much trop-strat mixing

showpage


SONEX EAtlantic
1997/10/07–1997/11/12
Pressure
CO[ppb]
O3[ppb]
C3H8[ppt]
H2O[ppm]
NOx[ppt]
PAN[ppt]
HNO3[ppt]
HNO3/NOx
PAN/NOx
Butane[ppt]
Relative Humidity[%]
log10(max(C2H6,1)/(C3H8+.5))

Conclusions Chemical Mechanisms:

Both observations and models show HCHO to have very broad continentental sources: CH_3CHO is in contrast more directly related to known source categories.

While CMAQ and other models may do reasonably well in simulating ozone, there are difficulties which limit our confidence in extrapolation (long distances, large changes in emissions types). Acetaldehyde (and PAN?) production are much too hot in models with very different reaction schemes, though over-prediction varies significantly.

The CMAQ-SAPRC and Langley models (Carbon-bond origin with considerable adaptation for global use) produce very large acetaldehyde in plumes.

Remaining Questions:
• Are poorly modeled alkoxy radical fates responsible for acetaldehyde overproduction?
• Are decisions involved in "lumping" for practical mechanisms to generous in assigning the acetaldehyde product?

HCHO is very strongly correlated with fine aerosol (indeed, aged aerosol number!) in both observations and this CMAQ model. Model organic nitrate and observed NOy are also strong correlates, but not for CH_3CHO. We interpret this to mean that formaldehyde responds to the net effect of all continental pollutant and natural emissions, while acetaldehyde is more limited to plumes.

Conclusions: Transport Effects on PAN

Transport effects are important:
FVGCM lofts PAN and precursors poorly, leading to low values;
GISS may still have difficulties with a "strat-trop mixed region"
DAO